# Europäisches Patentamt European Patent Office

Office européen des brevets



(11) EP 0 927 753 A1

(12)

## **EUROPEAN PATENT APPLICATION**

(43) Date of publication: 07.07.1999 Bulletin 1999/27

(51) Int. Cl.6: C09K 19/54, G02F 1/1333

(21) Application number: 98124536.8

(22) Date of filing: 22.12.1998

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU

MC NL PT SE

Designated Extension States:

AL LT LV MK RO SI

(30) Priority: 29.12.1997 IT MI972881

(71) Applicant: Sniaricerche S.C.P.A. I-75010 Pisticci Scalo (IT) (72) Inventors:

- Hakemi, Hassan-Ali
   20035 Lissone (MI) (IT)
- Santangelo, Michele 75019 Tricarico (MT) (IT)
- (74) Representative:
  Forattini, Amelia et al
  c/o Internazionale Brevetti
  Ingg. ZINI, MARANESI & C. S.r.I.
  Piazza Castello 1
  20121 Milano (IT)

## (54) Liquid crystal dispersed polymer electrooptical films having reverse morphology

(57) The invention provides a liquid crystal dispersed polymer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and the liquid crystal material has cholesteric properties. The invention also provides a liquid crystal dispersed poly-

mer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and substantially no memory effect. Methods for making these electrooptical films are also provided.

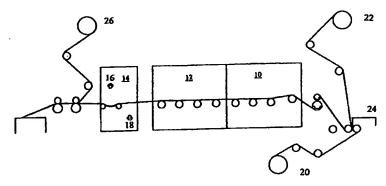


Fig. 1

## Description

#### Field of the Invention

[0001] The present invention relates to liquid crystal dispersed polymer (LCDP) electrooptical films. These LCDP electrooptical films comprise a discontinuous polymer phase dispersed in a continuous liquid crystal phase.

## Background of the invention

[0002] Polymer dispersed liquid crystal (PDLC) electrooptical films are known. See U.S. Patent No. 4,435,047 to Fergason. In a PDLC electrooptical film a discontinuous liquid crystal phase is dispersed in a continuous polymer phase. PDLC electrooptical films can be used in switchable windows, light modulators, displays, and other types of devices to control light transmission.

[0003] Composites of liquid crystals dispersed in a polymer matrix, such as polymer dispersed liquid crystal (PDLC) and nematic curvilinearly aligned phase (NCAP) devices, generally comprise droplets of a biaxially birefringent, nematic liquid crystal material dispersed in a transparent polymeric matrix. Such devices are of interest because they can be electrically controlled or switched between relatively translucent (i.e., light scattering or nearly opaque) and relatively transparent (i.e., light transmitting) states. This switching is possible because the liquid crystal droplets exhibit birefringence, i.e., optical anisotropy. All liquid crystals have two indices of refraction: an extraordinary index of refraction measured along the long axis of the rigid rodlike liquid crystals, and a smaller ordinary index of refraction measured in a plane perpendicular to the long axis. As a result, the droplets strongly scatter light when they are randomly oriented in the matrix and the devices appear translucent (or nearly opaque). On the application of either an electric field or a magnetic field, however, the long axes of the liquid crystal droplets become aligned along the direction of the electric/magnetic field vector and more directly transmit light.

[0004] If the refractive indices of the liquid crystal material and the polymer matrix are closely matched while in the field-induced, aligned state, the devices appear transparent. Thus, upon the application of an electric or magnetic field, for example, the device switches from a state in which it appears translucent (nearly opaque) to a state in which it appears transparent. Upon removal of the electrical or magnetic field, the device reverts to a translucent (opaque) state.

[0005] Devices containing composites of liquid crystals dispersed in a polymer matrix have been used as light valves, filters, shutters, information displays, and in architectural glass and windows.

[0006] In scientific investigations of PDLC technology, a phenomenon known as reverse morphology or microsphere morphology has been mentioned infrequently. In a reverse morphology system the polymer phase is dispersed in a continuous liquid crystal phase. Reverse morphology systems are more difficult to use than typical PDLC systems because the liquid crystal phase is not neatly encapsulated within the polymer phase and there often is less polymer to provide strength to the film in a reverse morphology system.

[0007] Reverse morphology systems have been described previously. Yamagishi et al., Proc. SPIE, 1080:24-31 (1989) describes a reverse morphology system having a nematic liquid crystal and a memory effect. Nomura et al., J. Appl. Phys., 68(6):2922-2926 (1990) describes an electrooptical film with a nematic liquid crystal component, connected polymer microspheres, and a memory effect. These documents do not disclose reverse morphology systems having no memory effect and they do not disclose reverse morphology systems with a liquid crystal having cholesteric properties.

[0008] In comparison with a traditional PDLC film with microdroplet morphology ("Swiss cheese" morphology, where the continuous phase is the polymer matrix and discontinuous phase is composed of liquid crystal microdroplets), a typical LCDP film with reverse morphology has the following advantages: (1) single-mode and dual-mode function (with cholesteric liquid crystal); (2) lower haze (both modes with cholesteric liquid crystal); (3) improvements in transparency, contrast ratio, and resistivity; and (4) less brittleness.

# Summary of the INVENTION

[0009] The invention provides a liquid crystal dispersed polymer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and the liquid crystal material has cholesteric properties; in this embodiment the electrooptical film can have a memory effect or substantially no memory effect. The invention also provides a liquid crystal dispersed polymer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and substantially no memory effect; in this embodiment the liquid crystal may have cholesteric or nematic properties.

[0010] The invention provides a method for producing a liquid crystal dispersed polymer electrooptical film comprising: (a) providing a mixture of a liquid crystal material and a prepolymer material; (b) curing the mixture with ultraviolet radiation; and (c) cooling the result of step (b), to form an electrooptical film with a reverse morphology.

## EP 0 927 753 A1

[0011] The invention also provides a method for producing a liquid crystal dispersed polymer electrooptical film comprising: (a) providing a mixture of a liquid crystal material and a prepolymer material; (b) cooling the mixture of step (a); and (c) curing the mixture of step (b) with ultraviolet radiation, to form an electrooptical film with a reverse morphology. [0012] Additional features and advantages of the invention are set forth in the description which follows and in part will be apparent from the description. The objectives and other advantages of the invention will be realized and attained by the LCDP films, their uses, and their methods of manufacture as particularly pointed out in the written description, claims, and appended drawings. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are intended to provide further explanation of the invention as claimed

## **BRIEF DESCRIPTION OF THE DRAWINGS**

## [0013]

10

25

30

35

- Fig. 1 shows the coater/laminator used in some of the Examples. ITO-PET film unwinds 20, 22, and 26 release the ITO-PET film. Unwinds 20 and 22 are used for dry lamination (SIPS-PIPS or
  - UV-PIPS) and unwinds 20 and 26 are used for wet lamination (TIPS). Temperature ovens 10 and 12 provide heat when necessary. UV oven 14 provides ultraviolet light and has UV lights 16 and 18. The liquid crystal prepolymer mixture is injected by injector 24.
- 20 Fig. 2 shows the morphology of the electrooptical film of Example 1.
  - Fig. 3 shows the morphology of the electrooptical film of Example 2.
  - Fig. 4 shows the morphology of the electrooptical film of Example 3.
  - Fig. 5 shows the morphology of the electrooptical film of Example 4.
  - Fig. 6 shows the morphology of the electrooptical film of Example 5.
  - Fig. 7 shows the morphology of the electrooptical film of Example 6.
  - Fig. 8 shows the morphology of the electrooptical film of Example 7.
  - Fig. 9 shows the morphology of the electrooptical film of Example 8.
  - Fig. 10 shows the morphology of the electrooptical film of Example 15.
  - Fig. 11 shows the transmission-voltage curves of the electrooptical film of Example 15.
  - Fig. 12 shows the morphology of the electrooptical film of Example 16.
    - Fig. 13 shows the transmission-voltage curves of the electrooptical film of Example 16.
    - Fig. 14 shows the transmission-voltage curves of the electrooptical film of Example 17.
    - Fig. 15 shows the transmission-voltage curves of the electrooptical film of Example 18.
    - Fig. 16 shows the transmission-voltage curves of the electrooptical film of Example 19.

# **DETAILED DESCRIPTION OF THE INVENTION**

- [0014] With particular reference to Figure 1, the mix is applied to a substrate based on ITO-PET, which is wound on a roll 20 before the application, is unwound from the roll 20 during the application, and is finally wound onto a second roll, not shown, after the setting of the mix. Generally, the mix is covered with a second substrate based on ITO-PET. The second substrate is wound on a third roll 22 before application, is unwound from the roll 22 during application, and is finally wound onto the second roll after the setting of the mix.
- [0015] The following text describes the preparation and fabrication process of liquid crystal dispersed polymer electrooptical films on rigid and flexible conductive supports using Polymerization Induced Phase Separation (PIPS) and Thermally Induced Phase Separation (TIPS) methods. The LCDP films were prepared by either a one step process (i.e., PIPS or TIPS) or a two step process (i.e., TIPS/PIPS, PIPS/TIPS). Thermoset, thermoplastic, and UV-curable polymers and nematic and cholesteric liquid crystals were used in the formulations and preparation processes.
- [0016] The film preparation procedures used were roll-to-roll coating and laminating techniques using either a lab coater or a pilot plant system.
- [0017] The invention provides a liquid crystal dispersed polymer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and the liquid crystal material has cholesteric properties. The liquid crystal material can comprise a nematic liquid crystal material and a chiral material; the liquid crystal material can comprise a chiral liquid crystal material. The liquid crystal material can comprise a cholesteric liquid crystal.
- 55 [0018] In one embodiment of the invention the electrooptical film has substantially no memory effect; in another embodiment of the invention the electrooptical film has a memory effect. In a preferred embodiment of the invention the electrooptical film has a contrast ratio greater than 10, more preferably than 12. In another embodiment the electrooptical film has a resistivity at 1000 Hz that is at least 50 percent greater than the resistivity of the comparison PDLC sam-

## EP 0 927 753 A1

ple of Example 10, preferably at least 75 percent greater than the resistivity of the comparison PDLC sample of . Example 10.

[0019] In one embodiment of the invention, the electrooptical film comprises greater than 20 percent by weight of polymer material relative to the total weight of liquid crystal material and polymer material. In other embodiments of the invention the electrooptical film comprises 30 percent or more by weight of polymer material; 40 percent or more by weight of polymer material; 50 percent or more by weight of polymer material.

[0020] The electrooptical film has a reverse morphology, but there are different types of reverse morphologies. In one embodiment of the invention, the electrooptical film has the macro phase separation morphology. An example of the macro phase separation is shown in Fig. 5. In another embodiment of the invention, the electrooptical film has the individual microsphere morphology. Examples of the individual microsphere morphology are shown in Figs. 3 and 4.

[0021] In still another embodiment of the invention, the electrooptical film has the substantially joined together microsphere morphology as shown in Figs. 6 and 7.

[0022] The electrooptical film can comprises spacers such as microspheres, microrods, or microfibers; in another embodiment, the electrooptical film does not comprise spacers. The microspheres formed in the method of the invention can substitute for spacers in certain embodiments of the invention. The electrooptical film can comprise a plastic sheet electrode, preferably at least two plastic sheet electrodes.

[0023] The invention also provides a liquid crystal dispersed polymer electrooptical film comprising a liquid crystal material and a polymer material in which the electrooptical film has a reverse morphology and substantially no memory effect.

20

[0024] In one embodiment of the invention, the electrooptical film comprises greater than 20 percent by weight of polymer material relative to the total weight of liquid crystal material and polymer material. In other embodiments of the invention the electrooptical film comprises 30 percent or more by weight of polymer material; 40 percent or more by weight of polymer material; 50 percent or more by weight of polymer material; 55 percent or more by weight of polymer material; or 60 percent or more by weight of polymer material.

[0025] In another embodiment of the invention, the liquid crystal material has cholesteric properties. The liquid crystal material having cholesteric properties can comprise a nematic liquid crystal material and a chiral material; the liquid crystal material having cholesteric properties can comprise a chiral liquid crystal material. The liquid crystal material having cholesteric properties can be a cholesteric liquid crystal. The liquid crystal material can have nematic properties; the liquid crystal material can comprise a nematic liquid crystal.

[0026] In a preferred embodiment of the invention the electrooptical film has a contrast ratio greater than 10, more preferably than 12. In another embodiment the electrooptical film has a resistivity at 1000 Hz that is at least 50 percent greater than the resistivity of the comparison PDLC sample of Example 10, preferably at least 75 percent greater than the resistivity of the comparison PDLC sample 10.

[0027] The electrooptical film can have the macro phase separation morphology, the individual microsphere morphology, or the substantially joined together microsphere morphology.

[0028] The electrooptical film can comprises spacers such as microspheres, microrods, or microfibers; in another embodiment, the electrooptical film does not comprise spacers. The microspheres formed in the method of the invention can substitute for spacers in certain embodiments of the invention. The electrooptical film can comprise a plastic sheet electrode, preferably at least two plastic sheet electrodes.

[0029] The invention provides a method for producing a liquid crystal dispersed polymer electrooptical film comprising: (a) providing a mixture of a liquid crystal material and a prepolymer material; (b) curing the mixture with ultraviolet radiation: and (c) cooling the result of step (b), to form an electrooptical film with a reverse morphology.

[0030] The invention also provides a method for producing a liquid crystal dispersed polymer electrooptical film comprising: (a) providing a mixture of a liquid crystal material and a prepolymer material; (b) cooling the mixture of step (a); and (c) curing the mixture of step (b) with ultraviolet radiation, to form an electrooptical film with a reverse morphology. [0031] In one embodiment of this method, the liquid crystal material has cholesteric properties. The liquid crystal material having cholesteric properties can comprise a nematic liquid crystal material and a chiral material; the liquid crystal material having cholesteric properties can comprise a chiral liquid crystal material.

[0032] In this method, the electrooptical film can have the macro phase separation morphology, the individual microsphere morphology, or the substantially joined together microsphere morphology. In one embodiment of this method, the electrooptical film has substantially no memory effect.

[0033] The invention also provides an electrooptical device comprising a source of electrical impulses and an electrooptical film of the invention, wherein the electrooptical film has a memory effect and the film is periodically subjected to an electrical impulse from the source to maintain the transparency or opacity of the film. Using the memory effect and periodic electrical impulses, the power consumption of the electrooptical device can be reduced.

[0034] Various phase separation processes can be used to make LCDP electrooptical films. Such phase separation processes include the following.